AD A 219 738

REPORT DOCUMENTATION PAGE	Form Approved OMB No. 0704-0188

1a. REPORT SECURITY CLASSIFICATION UNCLASSIFIED	1b. RESTRICTIVE MARKINGS

2a. SECURITY CLASSIFICATION AUTHORITY	3. DISTRIBUTION/AVAILABILITY OF REPORT
2b. DECLASSIFICATION/DOWNGRADING SCHEDULE	Approved for public release; distribution is unlimited.

4. PERFORMING ORGANIZATION REPORT NUMBER(S)	5. MONITORING ORGANIZATION REPORT NUMBER(S)
CRDEC-CR-042	

6a. NAME OF PERFORMING ORGANIZATION	6b. OFFICE SYMBOL (If applicable)	7a. NAME OF MONITORING ORGANIZATION
Kent State University		

6c. ADDRESS (City, State, and ZIP Code)	7b. ADDRESS (City, State, and ZIP Code)
Kent, OH 44242	

8a. NAME OF FUNDING/SPONSORING ORGANIZATION	8b. OFFICE SYMBOL (If applicable)	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER
CRDEC	SMCCR-RS	DAAA15-85-C-0019

8c. ADDRESS (City, State, and ZIP Code)	10. SOURCE OF FUNDING NUMBERS			
	PROGRAM ELEMENT NO.	PROJECT NO.	TASK NO.	WORK UNIT ACCESSION NO.
Aberdeen Proving Ground, MD 21010-5423				

11. TITLE (Include Security Classification)

New Aspects of Liquid Crystals and Foams in Decontamination

12. PERSONAL AUTHOR(S)
Acree, William E., Jr., and Brown, Glenn H.

13a. TYPE OF REPORT	13b. TIME COVERED	14. DATE OF REPORT (Year, Month, Day)	15. PAGE COUNT
Contractor	FROM 85 May TO 86 May	1990 January	34

16. SUPPLEMENTARY NOTATION

COR: Joseph W. Hovanec, SMCCR-RS, (301) 671-2761

17. COSATI CODES			18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)
FIELD	GROUP	SUB-GROUP	Decontamination; Liquid crystals
15	06	03	Hydrolysis; Foams. Dr
			Catalysis;

19. ABSTRACT (Continue on reverse if necessary and identify by block number)

Pseudo first order rate constants are reported for the dephosphorylation of diethyl 4-nitrophenylphosphate in several micellar and liquid crystalline solvent systems at pH of 12 to 13 and 25 °C. These measurements indicate that cationic surfactants enhance the hydrolysis of diethyl 4-nitrophenylphosphate, while anionic surfactants inhibit the chemical reaction. Rate constants for the dephosphorylation of the chemical agent simulant in a series of aqueous hexadecyltrimethylammonium hydroxide/hexadecyltrimethylammonium hydroxide liquid crystalline solvents were not significantly different than the rate constant in micellar hexadecyltrimethylammonium hydroxide solution. There was no overwhelming experimental evidence to recommend the more concentrated surfactant solutions over micellar solutions in the decontamination of chemical agents. The merits of foams as decontamination media are discussed. Preliminary kinetic measurements reveal that foamed didodecyldimethylammonium hydroxide surfactant solutions enhance the dephosphorylation of diethyl 4-nitrophenylphosphate, though the observed enhancement is not as large as in the corresponding unfoamed micellar solvent.

20. DISTRIBUTION/AVAILABILITY OF ABSTRACT	21. ABSTRACT SECURITY CLASSIFICATION
☒ UNCLASSIFIED/UNLIMITED ☐ SAME AS RPT ☐ DTIC USERS	UNCLASSIFIED

22a. NAME OF RESPONSIBLE INDIVIDUAL	22b. TELEPHONE (Include Area Code)	22c. OFFICE SYMBOL
SANDRA J. JOHNSON	(301) 671-2914	SMCCR-SPS-T

DD Form 1473, JUN 86 — Previous editions are obsolete

PREFACE

The work described in this report was authorized under Contract No. DAAA15-85-C-0019. This work was started in May 1985 and completed in May 1986.

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CONTENTS

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NEW ASPECTS OF LIQUID CRYSTALS AND FOAMS IN DECONTAMINATION

INTRODUCTION

Decontamination requires the rapid dispersal of an oxidizing or hydrolyzing solution, followed by rapid absorption and neutralization of the chemical agent. Mixtures of surfactants with water form molecularly organized systems capable of concentrating chemical agent solutes in the hydrophobic interior or near the polar-apolar interface, depending on the chemical nature of the solute. The chemical agent is thus confined and can undergo neutralization in the ordered media.

Kinetic studies in aqueous surfactant systems is a rapidly expanding area. Rate acceleration or inhibition of organic reactions in micellar solutions results from different rates of reaction of the substrate in the micellar phase and in the bulk solution, as well as substrate distribution between these two phases. In general, rate effects can be attributed to electrostatic and hydrophobic interactions between substrate and surfactant aggregate. Cationic micelles will enhance rates of reaction of nucleophilic anions with uncharged substrates while anionic micelles retard them. Nonionic and zwitterionic micelles should have little or no effect on reaction rates based on simple electrostatic considerations. Specific examples reported in the literature include rate enhancement in both the basic hydrolysis of esters by cationic micellar surfactants and the acid hydrolysis of orthoesters by anionic micelles.

Micellar catalysis tends to be more pronounced for surfactants having longer alkyl chains. Rate of hydrolysis of methyl orthobenzoate in aqueous micellar sodium alkyl sulfate solutions increase with increasing alkyl chain length. The effect of chain length can be rationalized by postulating increased charge density of the ions at the micellar surface with increasing carbon length which in turn would tend to increase the electric field around the reaction site.

Lyotropic liquid crystals are essentially extended micellar phases. They have many of the features which make micelles and vesicles so interesting for reactions and solubilizations. Because they are concentrated detergent-like solutions,

lyotropic liquid crystals sometimes can solubilize up to 100-fold more organic material than do conventional micellar media. Surprisingly, relatively few papers had been published in the chemical literature prior to this report. Ahmed and Friberg[1] studied the hydrolysis of p-nitrophenyl laurate in the lyophase water-hexadecyltrimethylammonium bromide (CTAB)-hexanol, and reported a pronounced increase in reaction rate. Bacon et al.[2] studied the hydrolysis of 4-substituted benzylidene t-butylamine N-oxides in dodecylammonium chloride-water and reported a pronounced decrease in reaction rate in the lamellar phase. Two later studies[3,4] showed that the hydrolysis rate constants for five 4-substituted benzylidene-t-butylamine N-oxides were reasonably correlated with octanol-water partition coefficients. Studies of oxidation of benzaldehyde in the liquid crystalline phase of an alkylbetaine-benzaldehyde-water indicated that the oxidation rate decreased in the lyophase.[5] A study of the hydrolysis of procaine hydrochloride, procaine methyl chloride and procaine ethyl chloride in a polyoxyethylene [6] tridecanol-water system in the lamellar phase indicated rate decrease.[6] The authors argued that the substrates are located within the extended micelle where they are presumably protected from hydrolytic bond cleavage. In general, kinetic studies in liquid crystalline media parallel those in ordinary and reversed micellar media. Localizing one reactant within a micelle will frequently protect from the hydrophilic environment, but if it is buried in the core of a reversed micelle containing an aqueous phase, reactivity will be enhanced.[7]

To gain a better understanding of chemical reactions in ordered media, we measured the rates of dephosphorylation of 0,0-diethyl 4-nitrophenylphosphate, the chemical agent simulant selected, in several liquid crystalline systems. Initial evaluation of the dephosphorylation reaction indicated that basic media proceeded faster. Attention was focused on aqueous surfactants that form ordered media in the range of pH 10-13.

EXPERIMENTAL STUDIES

Rates of dephosphorylation were determined by monitoring the formation of the phenolate ion spectrophotometrically at 400 nm. The reaction mechanism is well documented in both aqueous and micellar solutions.[7,8] Diethyl 4-nitrophenylphosphate was purchased from commercial sources and used without further purification. Stock solutions of the solute were prepared in dioxane/water (60% dioxane by volume) and injected directly into cuvette, the final concentration being approximately 10^{-4} M.

The basic hydrolysis produced an initial jump in the differential absorbance, followed by a gradual increase in absorbance. A linear plot of Ln $(A_\infty-A_t)$ vs time, ignoring the initial jump, suggested that the reaction is pseudo-first order in diethyl 4-nitrophenylphosphate. Rate constants were calculated through linear least squares analysis of the data, and were reproducible to $\pm10\%$. Uncertainties of this magnitude are to be expected in liquid crystalline media. The solutions are often viscous and contain both isotropic and molecularly ordered regions, as viewed under a dark stage polarized light microscope.

Specific systems attempted were: aqueous hexadecyltrimethylammonium hydroxide, aqueous sodium decylsulfate, aqueous potassium oleate, aqueous hexadecyltrimethylammonium bromide-1-hexanol, aqueous nonylphenoxypolyoxy-ethylene ethanol (a nonionic surfactant; marketed as IGEPAL CO-530 by GAF), aqueous sodium dodecylsulfate-1-decanol, and aqueous Aerosol OT. The latter five solvents were not used in the kinetic studies because of turbidity, high viscosity or lock of chemical stability near a pH of 12. The spectrophotometric method of analysis required that the solvent be optically transparent near 400 nm. Furthermore, air bubbles became trapped in the more viscous solvents, leading to erroneously high absorbances.

As reference points in the dephosphorylation of diethyl 4-nitrophenylphosphate, rate constants were also determined in aqueous sodium hydroxide solutions. Kinetic measurements were made at four different basicities in order to establish a rate *vs* pH profile for subsequent comparisons.

The various solvent systems were prepared from commercially available surfactants, alcohols, and HPLC grade distilled water. Hexadecyltrimethyl-ammonium hydroxide, didodecyldimethylammonium hydroxide and ditetradecyldimethylammonium hydroxide were prepared from the corresponding bromides *via* ion exchange. Surfactant concentrations were determined by non-aqueous titration (90% methanol/10% water by volume) against a freshly standardized HCl solution. The basicity of the solution was deliberately kept high so that a constant pH could be maintained without the use of buffers.

Experimental results are summarized in Table I for the 11 solvents studied. The reported rate constants represent the averages of at least three independent measurements. Absorbance data for representative kinetic runs are listed in Tables II-XIII.

DISCUSSION OF KINETIC RESULTS

Rate constants for the dephosphorylation of diethyl 4-nitrophenylphosphate in aqueous sodium hydroxide solution are a function of hydroxide ion concentration. Enhancement in rate of reaction is observed with increasing pH, as shown in Table I. To a first approximation, the rate appears to be first order in hydroxide ion in the pH range studied.

The rate constant data clearly show that anionic surfactants inhibit the rate of dephosphorylation. The observed pseudo-first order rate constant of 5.4×10^{-5} sec^{-1} in aqueous sodium decylsulfate (cmc concentration of surfactant) is approximately 12 times smaller than the value of 8.6×10^{-4} sec^{-1} (value is 6.8×10^{-4} sec^{-1} if corrected to a pH of 12.2) observed in the aqueous solution at approximately the same pH. Cationic

surfactants enhance reactivity as shown by the rate constant of 1.1×10^{-2} sec^{-1} in aqueous hexadecyltrimethylammonium hydroxide (cmc) compared to an interpolated value of 4.3×10^{-3} sec^{-1} for aqueous solutions at a pH of 13.0. Addition of hexadecyltrimethylammonium hydroxide to the aqueous micellar solution increases the rate slightly, a rate constant of 2.0×10^{-2} sec^{-1} was obtained for a 0.048 molar solution at pH of 13.1. This appears to be similar to the dephosphorylation of 4-nitrophenyl diphenylphosphate in micellized hexadecyltrimethylammonium hydroxide which shows the rate constants do not become constant when substrates are fully micellar bound and increase on addition of sodium hydroxide.[9]

Cationic surfactants known to exhibit unique behavior in water are the alkylammonium hydroxides. For example, aqueous dispersions of dialkyldimethyl-ammonium hydroxide form vesicles spontaneously. The vesicles are believed to be a spherical structure containing a bilayer arrangement of ordered surfactant and water molecules. Dialkyldimethylammonium hydroxides are extremely soluble in water, while the corresponding halides are sparsely soluble. The addition of sodium hydroxide to aqueous dialkyldimethylammonium hydroxide dispersions give clear solutions up to 0.5 molar. The vesicles grow and flocculate with the addition of salts. Video-enhanced contrast polarization microscopy shows vesicles comparable in size with 1000 Å latex spheres in solution.[10] These monlayer spheres represent a large interfacial area that may serve for decontamination reactions.

The rate constant for the dephosphorylation reaction in both aqueous didodecyldimethylammonium hydroxide and ditetradecyldimethylammonium hydroxide dispersions is eight times the value obtained in aqueous solutions. Vesicles were experimentally observed by us in the two more concentrated solutions with Normarski Differential Microscopy. Rate constants in 0.0124 molar and 0.0620 molar didodecyldimethylammonium hydroxide do suggest possible enhancement with increasing surfactant concentration. though both values are identical within

experimental uncertainty. Measurements at lower pH may prove to be more definitive. For the moment, there appears to be no overwhelming evidence to suggest recommending this more concentrated surfactant media in decontamination. It is more expensive to prepare.

Alkylammonium halides are less soluble in water, and formation of a liquid crystalline mesophase might be possible through acid neutralization of the corresponding hydroxide. Neutralization of hexadecyltrimethylammonium hydroxide with aqueous hydrobromic acid is expected to form different liquid crystalline mesophases depending upon the concentration of bromide present. Four different solutions, ranging from 65% to 40% neutralized, were prepared for use as solvent media. Examination of these solutions microscopically indicated the presence of the hexagonal liquid crystalline mesophase. It was hoped that the ordered mesophases would provide favorable orientation of the phosphate molecules at the boundary between the micellar water phase and the surfactant layer as well as exerting a large electrostatic effect thereby influencing the rate of hydrolysis.[11] Rate constants for the dephosphorylation in the series of hexadecyltrimethylammonium bromide/hexadecyltrimethylammonium hydroxide solvents, however, were not significantly faster than those obtained with aqueous micellar hexadecyltrimethylammonium hydroxide at the cmc. The observed two-fold increase in the dephosphorylation rate in aqueous hexadecyltrimethylammonium hydroxide (0.293 M) + hexadecyltrimethylammonium bromide (0.192 M) solvent is in all likelihood attributable to the increased pH.

Rate constants for the dephosphorylation reaction in the series of hexadecyltrimethylammonium hydroxide + hexadecyltrimethylammonium bromide were not significantly different than the rate constant in micellar hexadecyltrimethylammonium hydroxide solution. This suggests that the liquid crystalline structures did not exert a large influence. It was also apparent from

microscopic examination of the solutions that the extent of liquid crystal formation in these highly basic solutions appeared to be much less than what is observed in neutral or acidic solutions of hexadecyltrimethylammonium bromide. Even at relatively low surfactant concentrations (10 to 11% hexadecyltrimethylammonium bromide) in neutral solutions a deformation to rod-like micelles results as shown by viscosity measurements, light scattering, conductance anisotropy and x-ray diffraction examinations.[12] The transition to the liquid crystalline mesomorphic state seems to depend mainly on the volume of micellar substance including only the directly bound water of hydration and this appears in the neutral solution at 25% aqueous hexadecyltrimethylammonium bromide.

FOAMS IN DECONTAMINATION

The contracted research also involved a literature survey regarding the merits and feasibility of foams in decontamination of chemical agents. Publications in this specific area were not found in the chemical literature. Several papers, [13-24] however, had been published on the application of foams to the control of hazardous chemical spills, particularly in regards to fire and vapor pressure suppression. The literature survey focused primarily on learning:

1. the current state-of-the-art in the use of foams in spill controls, and

2. the limitations and restrictions for foam usage on spills,

with the expectation that this information would be extendable to chemical agents.

Foams used to control chemical spills are either protein or surfactant based. Protein based foaming agents are only applicable in the generation of low expansion foams, less than a 30:1 expansion ratio. The expansion ratio is a dimensionless number expressing the ratio of the volume of foam to that of the liquid solution from which it was generated. Surfactant foams can provide a much larger range of expansions, with ratios up to 1500:1. Surfactant-based foams have an added advantage in the possible decontamination of chemical agents. Collapse of the foam

13

will give a thin aqueous layer of surfactant solutions. Aqueous solutions of cationic surfactants do enhance the dephosphorylation of diethyl 4-nitrophenylphosphate.

Low expansion foams are usually made *via* mechanical agitation and practical expansions are in the range of 3:1 to 8:1. Low expansion foams, by their nature, are less influenced by atmospheric effects of wind, rain, or high temperature. In terms of vapor mitigation they will provide the longest time delay before vapor breakthrough occurs. Takimoto, Lewis, and Hiltz[23] reported that a single application of a low expansion foam, prepared from a Rohm & Haas ASE 95/MSAR surfactant combination, could effectively cover a chemical spill of monomethylhydrazine for over four hours.

High expansion foams use about one half the water volume for equivalent cover as low expansion. Equivalent cover is achieved through greater foam height. High expansion foams are generated by impaction of foam on a screen or net. Blowing air is introduced either by a fan or through aspiration of water spray. Practical expansions are reported to range from 250:1 to 1000:1. The use of high expansion foams is governed by both wind conditions and the nature of the spilled material. Below wind speeds of 10 miles per hour, maintenance of an adequate high expansion foam blanket should be possible.

The performance of a specific foam system depends, to a large extent, on the expansion ratio, depth of coverage and the nature of the hazardous material to be covered. An appraisal of the capability of foams for spill control was conducted under EPA sponsorship.[22] The study showed that foam blankets could be developed over most chemicals; the principal exceptions were polar solvents and those which affected a change in pH. A pectin modified foam showed applicability on a broad range of chemicals.

Stability and vapor suppression comparisons indicate that low expansion foams are generally more effective than the corresponding high expansions. For example,

tests conducted by MSA Research Corporation, funded by the Air Force, showed that low expansion foams (5:1 through 20:1 expansion ratio) were effective when applied in layers between 4-6 inches and could be effective over rocket fuel for more than four hours. High expansion foams (100:1 through 150:1 expansion ratio) required a layer depth of at least 12 inches to provide the same degree of control as low expansion, and must be replenished periodically if four hour control is desired.[19]

Foams can provide short-term protection over chemical agents, but their lifetime is for only a definite period. All volatile materials will have some degree of permeability through foam. It is doubtful that foams can provide any significant sustained degree of protection against chemical agents, unless a specific system can be developed which will both cover and chemically neutralize the agent. The possibility exists for developing a foam blanket that neutralizes chemical agents as foams can be prepared using cationic/anionic surfactants. Foams do offer large surface areas for reactions.

As an extension of our literature evaluation of foams, we did attempt kinetic dephosphorylation rate measurements in aqueous didodecyldimethylammonium hydroxide foams at 0.0124 molar surfactant concentration and pH of 11.0. The foams were prepared and maintained by mechanical agitation and by bubbling nitrogen through the solution. Early measurements were made on foams prepared by bubbling air through the solution, but it was discovered that this method introduced carbon dioxide which lowered the pH. The foam was permitted to collapse and the measured absorbance of the foamed system, excluding foams prepared by bubbling air, was always between 45 and 75% of an identically prepared unfoamed system. Absorbance measurements indicate that the rate of hydrolysis is faster in the absence of the foam. Absorbances in both the foamed and unfoamed didodecyldimethylammonium hydroxide solvents were greater than that in a third aqueous solvent, also at pH of 11.0. Reaction times ranged from 2 to 5 hours. Only a

15

single foam system was studied, and in all likelihood it should be possible to devise a better system for enhancing the rate of dephosphorylation of diethyl 4-nitrophenylphosphate. The development of foams and their application in chemical agent decontamination is an area that should receive further considerations.

Table I. Rate Constants for the Dephosphorylation of Diethyl 4-Nitrophenylphosphate in Various Solvent Media at 25°C

Solvent Media	Molarity	NaOH	pH[a]	Average Rate Constant[b]
Water		yes	12.3	8.57×10^{-4}
		yes	12.6	1.60×10^{-3}
		yes	12.9	3.51×10^{-3}
		yes	13.2	6.84×10^{-3}
Sodium Decylsulfate	cmc	yes	12.2	5.45×10^{-5}
Hexadecyltrimethylammonium Hydroxide	cmc	yes	13.0	1.14×10^{-2}
Hexadecyltrimethylammonium Hydroxide	0.048	yes	13.1	2.01×10^{-2}
Hexadecyltrimethylammonium Hydroxide +	0.168	no	13.0	1.01×10^{-2}
Hexadecyltrimethylammonium Bromide	0.317			
Hexadecyltrimethylammonium Hydroxide +	0.246	no	13.2	1.22×10^{-2}
Hexadecyltrimethylammonium Bromide	0.239			
Hexadecyltrimethylammonium Hydroxide +	0.255	no	13.3	1.54×10^{-2}
Hexadecyltrimethylammonium Bromide	0.230			
Hexadecyltrimethylammonium Hydroxide +	0.293	no	13.3	2.28×10^{-2}
Hexadecyltrimethylammonium Bromide	0.192			
Didodecyldimethylammonium Hydroxide[c]	0.0620	no	12.3	9.61×10^{-3}
Didodecyldimethylammonium Hydroxide	0.0124	yes	12.0	4.20×10^{-3}
	0.0124	yes	12.3	7.91×10^{-3}
Ditetradecyldimethylammonium Hydroxide[c]	0.0410	yes	12.3	8.50×10^{-3}

a pH measurements ± 0.02.

b Pseudo-first order rate constant, see [1].

c Didodecyldimethylammonium hydroxide and ditetradecyldimethylammonium hydroxide prepared from the corresponding bromide and concentration determined by titration.

17

Table II

Absorbance Values for the Basic Hydrolysis of Diethyl 4-Nitrophenyl
Phosphate in Aqueous Didodecyldimethylammonium
Hydroxide Dispersions (0.062M) at pH = 12.3 and 400 nM.

Time (min)	A_t	$A_\infty - A_t$	$\ln(A_\infty - A_t)$
0.42	0.404	0.956	-0.045
0.92	0.608	0.752	-0.285
1.40	0.800	0.560	-0.580
1.90	0.920	0.440	-0.821
2.42	1.008	0.352	-1.044
2.92	1.096	0.264	-1.332
3.42	1.160	0.200	-1.609
3.92	1.200	0.160	-1.833
4.42	1.240	0.120	-2.120
4.92	1.264	0.096	-2.343
5.42	1.288	0.072	-2.631
6.42	1.328	0.032	-3.442
7.42	1.344	0.016	-4.135
8.42	1.360	0.000	- - -

Calculated rate constant of 9.418×10^{-4} sec^{-1}

A_t refers to the differential absorbance at time = t.

A_∞ refers to the differential absorbance after the reactant has been completely
consumed, t = ∞.

Table III
Absorbance Value for the Basic Hydrolysis of Diethyl 4-Nitrophenyl Phosphate in Aqueous Didodecyldimethylammonium Hydroxide Dispersions (0.062M) at pH = 12.3 and 400 nM.

Time (min)	At	$A_\infty - A_t$	$\ln (A_\infty - A_t)$
0.37	0.432	0.948	-0.053
0.62	0.560	0.820	-0.198
0.87	0.630	0.750	-0.288
1.12	0.772	0.608	-0.498
1.37	0.860	0.520	-0.654
1.62	0.932	0.448	-0.803
1.87	0.994	0.386	-0.952
2.12	1.052	0.328	-1.115
2.37	1.088	0.292	-1.231
2.62	1.124	0.256	-1.363
2.87	1.160	0.220	-1.514
3.12	1.188	0.192	-1.650
3.37	1.212	0.168	-1.784
3.62	1.236	0.144	-1.938
3.87	1.248	0.132	-2.025
4.12	1.272	0.108	-2.226
4.37	1.288	0.092	-2.386
4.87	1.312	0.068	-2.688
5.37	1.328	0.052	-2.956
6.37	1.352	0.028	-3.576
7.37	1.364	0.018	-4.135
8.37	1.372	0.008	-4.828
	1.380	(after 24 hours)	

Calculated rate constant of 9.81×10^{-3} sec

TABLE IV

Absorbance Values of the Basic Hydrolysis of Diethyl 4-Nitrophenyl Phosphate in Aqueous Solutions at pH = 12.3 and 400 nM

Time (min)	A_t	$A_\infty - A_t$	$\ln(A_\infty - A_t)$
0.34	0.238	1.272	0.241
0.84	0.256	1.254	0.226
1.34	0.288	1.222	0.200
1.84	0.316	1.194	0.177
2.34	0.336	1.174	0.160
2.84	0.360	1.150	0.140
3.34	0.380	1.130	0.122
3.84	0.400	1.110	0.104
4.34	0.424	1.086	0.083
4.84	0.448	1.062	0.060
5.34	0.472	1.038	0.037
5.84	0.492	1.018	0.018
6.84	0.536	0.974	-0.026
7.84	0.578	0.932	-0.070
8.84	0.616	0.894	-0.112
9.84	0.648	0.862	-0.149
10.84	0.684	0.826	-0.191
11.84	0.720	0.790	-0.236
12.84	0.748	0.762	-0.272
13.84	0.780	0.730	-0.315
14.84	0.812	0.698	-0.360
15.84	0.840	0.670	-0.400

Table IV (cont'd)

Time (min)	A_t	$A_\infty - A_t$	$\ln (A_\infty - A_t)$
16.84	0.872	0.638	-0.449
17.84	0.896	0.614	-0.488
19.84	0.952	0.558	-.0.583
21.84	0.992	0.518	-0.658
23.84	1.036	0.474	-0.747
25.09	1.056	0.454	-0.790
27.09	1.096	0.414	-0.882
29.09	1.128	0.382	-0.962
31.09	1.160	0.350	-1.050
33.09	1.188	0.322	-1.133
37.09	1.240	0.270	-1.309
41.09	1.284	0.226	-1.487
45.09	1.320	0.190	-1.661
49.09	1.352	0.158	-1.845
53.09	1.384	0.126	-2.071
57.09	1.404	0.106	-2.244
61.09	1.424	0.086	-2.453
65.09	1.440	0.070	-2.659
69.09	1.456	0.054	-2.919
77.09	1.480	0.030	-3.507
85.09	1.492	0.018	-4.017
93.09	1.506	0.004	-5.521
133.9	1.510	0.000	- - -

rate constant of 8.364×10^{-2} sec

TABLE V

Absorbance Values for the Basic Hydrolysis of Diethyl 4-Nitrophenyl Phosphate in Aqueous Hexadecyltrimethylammonium Hydroxide (0.255 M) + Hexadecyltrimethylammonium Bromide (0.230 M) Solvent Media at a pH of 13.3 and 400 nm

Time (min)	A_t	$A_\infty - A_t$	$\ln (A_\infty - A_t)$
0.41	0.264	1.231	0.208
1.41	0.312	1.183	0.168
2.41	0.360	1.135	0.127
3.41	0.408	1.087	0.083
4.41	0.448	1.047	0.046
5.41	0.492	1.003	0.003
6.41	0.532	0.963	-0.038
7.41	0.571	0.923	-0.080
8.41	0.608	0.887	-0.120
9.41	0.648	0.847	-0.166
10.41	0.684	0.811	-0.209
11.41	0.712	0.783	-0.245
12.41	0.748	0.747	-0.292
14.41	0.812	0.683	-0.381
16.41	0.872	0.623	-0.473
18.41	0.924	0.571	-0.560
20.41	0.970	0.525	-0.644
22.41	1.016	0.479	-0.736
24.41	1.054	0.441	-0.819
26.41	1.088	0.407	-0.899
28.41	1.120	0.375	-0.981

Table V (cont'd)

Time (min)	A_t	$A_\infty - A_t$	$\ln(A_\infty - A_t)$
30.41	1.154	0.341	-1.076
32.41	1.180	0.315	-1.155
34.41	1.208	0.287	-1.248
36.41	1.236	0.259	-1.351
40.41	1.276	0.219	-1.519
44.41	1.314	0.181	-1.709
48.41	1.344	0.151	-1.890
52.41	1.376	0.119	-2.129
56.41	1.398	0.097	-2.333
60.41	1.418	0.077	-2.564
64.41	1.436	0.059	-2.830
68.41	1.444	0.051	-2.976
72.41	1.460	0.035	-3.352
76.41	1.474	0.021	-3.863
80.41	1.480	0.015	-4.200
84.41	1.488	0.007	-4.962
146.41	1.495	0.000	- - -

rate constant of 8.776×10^{-4} sec^{-1}

23

TABLE VI

Absorbance Values for the Basic Hydrolysis of Diethyl 4-Nitrophenyl Phosphate in Aqueous Hexadecyltrimethylammonium Hydroxide (0.255 M) + Hexadecyltrimethylammonium Bromide (0.230 M) Solvent Media at a pH of 13.3 and 400 nm

Time (min)	A_t	$A_\infty - A_t$	$\ln (A_\infty - A_t)$
0.37	0.408	0.799	-0.224
0.62	0.562	0.645	-0.439
0.87	0.684	0.523	-0.648
1.12	0.782	0.425	-0.856
1.37	0.868	0.339	-1.082
1.62	0.938	0.269	-1.313
1.87	0.990	0.217	-1.528
2.12	1.030	0.177	-1.732
2.37	1.066	0.141	-1.959
2.62	1.092	0.115	-2.163
2.87	1.114	0.093	-2.375
3.12	1.132	0.075	-2.590
3.37	1.140	0.067	-2.703
3.62	1.163	0.044	-3.124
3.87	1.171	0.036	-3.324
4.12	1.174	0.033	-3.411
4.37	1.184	0.023	-3.772
4.62	1.188	0.019	-3.963
5.12	1.192	0.015	-4.200
5.62	1.196	0.011	-4.510
6.12	1.203	0.004	-5.521

$A_\infty = 1.207$

rate constant $= 1.4519 \times 10^{-2} \sec^{-1}$

TABLE VII

Absorbance Values for the Basic Hydrolysis of Diethyl 4-Nitrophenyl Phosphate in Aqueous Hexadecyltrimethylammonium Hydroxide (0.255 M) + Hexadecyltrimethylammonium Bromide (0.230 M) Solvent Media at a pH of 13.3 and 400 nm

Time (min)	A_t	$A_\infty - A_t$	$\ln(A_\infty - A_t)$
0.35	0.400	0.815	-0.205
0.60	0.576	0.639	-0.448
0.85	0.704	0.511	-0.671
1.10	0.804	0.411	-0.889
1.35	0.888	0.327	-1.118
1.60	0.956	0.259	-1.351
1.85	1.014	0.201	-1.604
2.10	1.054	0.161	-1.826
2.35	1.080	0.135	-2.002
2.60	1.112	0.103	-2.273
2.85	1.136	0.079	-2.538
3.10	1.152	0.063	-2.765
3.35	1.160	0.055	-2.900
3.60	1.176	0.039	-3.244
3.85	1.182	0.033	-3.418
4.10	1.192	0.023	-3.772
4.35	1.197	0.018	-4.014
4.60	1.200	0.015	-4.200
4.85	1.204	0.011	-4.510
5.35	1.210	0.005	-5.298

$A_\infty = 1.215$

rate constant $= 1.617 \times 10^{-2}\ \mathrm{sec}^{-1}$

TABLE VIII

Absorbances for the Hydrolysis of Diethyl 4-Nitrophenyl Phosphate in Aqueous Hexadecyltrimethylammonium Hydroxide (0.168 M) + Hexadecyltrimethyl-ammonium Bromide (0.317 M) Solvent Media at a pH of 13.0 and 400 nm

Time (min)	A_t	$A_\infty - A_t$	$\ln (A_\infty - A_t)$
0.30	0.456	1.374	0.318
0.55	0.612	1.218	0.197
0.80	0.760	1.070	0.068
1.05	0.880	0.950	-0.051
1.30	0.996	0.834	-0.182
1.55	1.092	0.738	-0.304
1.80	1.168	0.662	-0.412
2.05	1.240	0.590	-0.528
2.30	1.304	0.526	-0.642
2.55	1.364	0.466	-0.764
2.80	1.420	0.410	-0.892
3.05	1.464	0.366	-1.005
3.55	1.544	0.286	-1.252
4.05	1.620	0.210	-1.561
4.55	1.648	0.182	-1.704
5.05	1.690	0.140	-1.966
5.55	1.720	0.110	-2.207
6.05	1.744	0.086	-2.453
6.55	1.768	0.062	-2.781
7.05	1.786	0.044	-3.124
7.55	1.800	0.030	-3.507
8.30	1.824	0.006	-5.116

$A_\infty = 1.830$

rate constant $= 9.310 \times 10^{-3}$ sec^{-1}

TABLE IX

Absorbances for the Hydrolysis of Diethyl 4-Nitrophenyl Phosphate in Aqueous Hexadecyltrimethylammonium Hydroxide (0.168M) + Hexadecyltri methylammonium Bromide (0.317 M) Solvent Media at a pH of 13.0 and 400 nm.

Time (min)	A_t	$A_\infty - A_t$	$\ell n (A_\infty - A_t)$
0.43	0.392	0.876	-0.132
0.68	0.488	0.780	-0.248
0.93	0.584	0.684	-0.380
1.18	0.664	0.604	-0.504
1.43	0.732	0.536	-0.624
1.68	0.800	0.468	-0.759
1.93	0.856	0.412	-0.887
2.18	0.908	0.360	-1.022
2.43	0.952	0.316	-1.152
2.68	0.992	0.276	-1.287
2.93	1.024	0.244	-1.411
3.43	1.088	0.180	-1.715
3.93	1.128	0.140	-1.966
4.43	1.160	0.108	-2.221
4.93	1.184	0.084	-2.477
5.43	1.212	0.056	-2.882
6.18	1.240	0.028	-3.576
6.93	1.254	0.014	-4.269
7.93	1.264	0.004	-5.521

$A_\infty = 1.268$

rate constant $= 1.090 \times 10^{-2} \, \text{sec}^{-1}$

TABLE X

Absorbance Values for the Basic Hydrolysis of Diethyl 4-Nitrophenyl Phosphate in Aqueous Hexadecyltrimethylammonium Hydroxide (CMC Concentration of Surfactant) Solvent Media at a pH of 13.0 and 400 nm

Time (min)	A_t	$A_\infty - A_t$	$\ln(A_\infty - A_t)$
0.34	0.448	0.802	-0.221
0.59	0.648	0.602	-0.507
0.84	0.780	0.470	-0.755
1.09	0.896	0.350	-1.038
1.34	0.968	0.282	-1.266
1.59	1.022	0.228	-1.478
1.84	1.076	0.174	-1.749
2.09	1.112	0.138	-1.981
2.34	1.143	0.107	-2.235
2.59	1.162	0.088	-2.430
2.84	1.184	0.066	-2.718
3.09	1.198	0.052	-2.957
3.34	1.202	0.048	-3.037
3.59	1.212	0.038	-3.270
3.84	1.218	0.032	-3.442
4.09	1.219	0.031	-3.474
4.34	1.222	0.028	-3.576
4.59	1.224	0.026	-3.650
5.34	1.228	0.022	-3.817
5.84	1.236	0.014	-4.269
6.34	1.239	0.011	-4.510

$A_\infty = 1.250$

Rate constant $= 1.194 \times 10^{-2}$ sec^{-1}

TABLE XI

Absorbance Values for the Basic Hydrolysis of Diethyl 4-Nitrophenyl Phosphate in
Aqueous Hexadecyltrimethylammonium Hydroxide (CMC
Concentration of Surfactant) Solvent at a pH of 13.0 and 400 nm

Time (min)	A_t	$A_\infty - A_t$	$\ln(A_\infty - A_t)$
0.38	0.466	0.789	-0.237
0.63	0.636	0.619	-0.480
0.88	0.770	0.485	-0.724
1.13	0.878	0.377	-0.976
1.38	0.952	0.303	-1.194
1.63	1.004	0.251	-1.382
1.88	1.056	0.199	-1.614
2.13	1.092	0.163	-1.814
2.38	1.120	0.135	-2.002
2.63	1.142	0.113	-2.180
2.88	1.160	0.095	-2.354
3.13	1.192	0.063	-2.765
3.38	1.198	0.057	-2.865
3.63	1.208	0.047	-3.058
3.88	1.215	0.040	-3.219
4.13	1.218	0.037	-3.297
4.63	1.220	0.035	-3.352
4.88	1.224	0.031	-3.474
5.38	1.229	0.026	-3.650
5.63	1.232	0.023	-3.772
6.38	1.235	0.020	-3.912

$A_\infty = 1.255$

Rate constant $= 1.081 \times 10^{-2}$ sec^{-1}

TABLE XII

Absorbance Values for the Basic Hydrolysis of Diethyl 4-Nitrophenyl
Phosphate in Aqueous Hexadecyltrimethylammonium Hydroxide
(0.048 M) at a pH of 13.1 and 400 nm

Time (min)	A_t	$A_\infty - A_t$	$\ln (A_\infty - A_t)$
0.32	0.488	0.716	-0.334
0.57	0.672	0.532	-0.631
0.82	0.820	0.384	-0.957
1.07	0.930	0.274	-1.295
1.32	1.000	0.204	-1.590
1.57	1.056	0.148	-1.911
1.82	1.096	0.108	-2.226
2.07	1.128	0.076	-2.577
2.32	1.148	0.056	-2.882
2.57	1.160	0.044	-3.124
2.82	1.176	0.028	-3.576
3.07	1.178	0.026	-3.650
3.32	1.188	0.016	-4.135
3.57	1.192	0.012	-4.423
3.82	1.196	0.008	-4.828
4.07	1.198	0.006	-5.116
4.32	1.200	0.004	-5.521
4.82	1.202	0.002	-6.215

$A_\infty = 1.204$

rate constant $= 2.150 \times 10^{-2} \sec^{-1}$

TABLE XIII

Absorbance Values for the Basic Hydrolysis of Diethyl 4-Nitrophenyl Phosphate in Aqueous Hexadecyltrimethylammonium Hydroxide (0.048 M) at a pH of 13.1 and 400 nm

Time (min)	A_t	$A_\infty - A_t$	$\ell n\,(A_\infty - A_t)$
0.31	0.544	0.681	-0.384
0.56	0.744	0.481	-0.732
0.81	0.896	0.329	-1.112
1.06	0.996	0.229	-1.474
1.31	1.064	0.161	-1.826
1.56	1.118	0.107	-2.235
1.81	1.158	0.067	-2.703
2.06	1.179	0.046	-3.079
2.31	1.180	0.045	-3.101
2.56	1.185	0.040	-3.219
2.81	1.198	0.027	-3.612
3.06	1.204	0.021	-3.863
3.31	1.206	0.019	-3.963
3.56	1.215	0.010	-4.605
3.81	1.219	0.006	-5.116
4.56	1.220	0.005	-5.298
5.31	1.222	0.003	-5.809

$A_\infty = 1.225$

rate constant $= 1.878 \times 10^{-2}\,\text{sec}^{-1}$

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